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(54) CATALYSEURS DE METALLOCENE IONIQUE SUR SUPPORT POUR LA POLYMERISATION D'OLEFINES
(54) SUPPORTED IONIC METALLOCENE CATALYSTS FOR OLEFIN POLYMERIZATION

(57)

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(54) **CATALYSEURS DE METALLOCENE IONIQUE SUR SUPPORT POUR LA POLYMERISATION D'OLEFINES**

(54) **SUPPORTED IONIC METALLOCENE CATALYSTS FOR OLEFIN POLYMERIZATION**

(57) Catalyseur supporté de polymérisation d'oléfines, comprenant un composant d'alliage organométallique du groupe IV-B ainsi qu'un composant d'activation ionique comprenant un cation capable de donner un proton, et un anion volumineux labile comportant une pluralité de radicaux lipophiles de sorte que l'anion est empêché stériquement de se lier de manière covalente à un cation produit par le métal du groupe IV-B de l'alliage organométallique.

(57) A supported catalyst for olefin polymerisation comprising a Group IV-B metallocene component and an ionic activator component comprising a cation capable of donating a proton and a labile bulky anion having a plurality of lipophilic radicals so that the anion is sterically hindered from covalently bonding with a cation produced from the Group IV-B metal of the metallocene.

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(57) Abstract

A supported catalyst for olefin polymerization comprising a Group IV-B metallocene component and an ionic activator component comprising a cation capable of donating a proton and a labile bulky anion having a plurality of lipophilic radicals so that the anion is sterically hindered from covalently bonding with a cation produced from the Group IV-B metal of the metallocene.

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SUPPORTED IONIC METALLOCENE CATALYSTS FOR OLEFIN POLYMERIZATION

Background of the Invention

1. Field of the Invention

The invention relates to supported catalysts for polymerization of olefins including gas or slurry phase polymerization of olefins, diolefins, cyclic olefins and acetylenically unsaturated monomers. These catalysts, which may be supported on known catalyst supports, include a Group IV-B metal metallocene compound and an ionic activator compound. While the homogeneous variant of this catalyst system has been previously disclosed in copending EPA 277004 a supported form of the catalyst system has not heretofore been produced. The supported catalyst, suitable for use in gas or slurry phase olefin polymerization, provides a polymer product having a narrower particle size distribution and higher bulk density than achievable with the homogeneous catalyst system. Furthermore, the use of the supported

catalyst in the gas phase results in greatly reduced reactor fouling as compared to the unsupported or homogeneous variant. By employing suitably sized supports, the catalyst system can be employed in solution and high pressure polymerization processes.

2. Background

Ziegler-Natta type catalysts for the polymerization of olefins are well known. The traditional Ziegler-Natta type systems comprise a metal halide activated to a catalyst species by reaction with a metal alkyl cocatalyst, particularly an aluminum alkyl cocatalyst. The activation of these traditional Ziegler-Natta catalysts generates a variety of different active sites. As a consequence of this non-uniformity of the active sites, the catalysts produce polymer products of broad molecular weight distribution (MWD). Furthermore, the copolymer products exhibit broad composition distribution (CD), poor comonomer incorporation and blocky sequence distribution.

Recently it has been found that active catalysts are formed when a bis(cyclopentadienyl) compound of the Group IV-B metals, in particular zirconium and hafnium, is activated by an alumoxane. The metallocene-alumoxane catalysts whether homogeneous or supported generally possess high activity and are more versatile than conventional Ziegler-Natta catalysts in that they may be effectively used to produce a variety of polymer products including, for example, high density linear polyethylene (HDPE), linear low density polyethylene (LLDPE), ethylene-propylene copolymer (EP), non-crystalline polypropylene and crystalline polypropylene. The metallocene-alumoxane catalysts also offer the significant advantage over the traditional Ziegler-Natta catalysts of being able to produce polymers with narrow MWD.

While the metallocene-alumoxane catalysts do offer significant advantages over the traditional Ziegler-Natta catalysts, they nevertheless have limitations in practical commercial applications. These limitations include the relatively high cost of the alumoxane cocatalysts. Alumoxane is also air sensitive and

difficult to manipulate. Furthermore, the metallocene-alumoxane catalysts, while producing a narrow MWD polymer product, have a limited capability to produce high molecular weight polymers or polymers having a high comonomer content.

Copending U.S. Patent Application Serial No. 133,480, also published as European Patent Application 277,004, describes a further advance in metallocene catalysts: a new metallocene catalyst which does not require either an alkyl aluminum or an alumoxane as an activator. The Group IV-B metallocene catalyst is prepared as a reaction product of a Group IV-B metal metallocene compound and an ionic activator compound. The ionic activator comprises a cation which will irreversibly react with at least one ligand contained in the Group IV-B metal metallocene compound and a labile bulky anion which is a single coordination complex having a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid atom, the bulk of said anion being such that upon reaction of the activator cation donatable proton with a proton reactable substituent of a bis(cyclopentadienyl) Group IV-B metal compound to form a Group IV-B metal cation, the anion of the activator is sterically hindered from covalently coordinating to the Group IV-B metal cation. Hence, as described in the copending application, an active catalytic species of a metallocene is formed, namely an ionic pair comprising a metallocene transition metal cation paired with a noncoordinating anion of the activator component.

The new metallocene catalyst system (hereafter referred to as an "ionic metallocene catalyst") eliminates the need for an expensive alumoxane activator. The ionic metallocene catalyst also offers other advantages over the metallocene-alumoxane catalysts such as permitting the production of polyolefin products of narrow MWD and of significantly higher weight average molecular weight at high rates of catalytic activity while also permitting better incorporation of comonomers and the control of the chain end chemistry of the polymer.

The new ionic metallocene catalyst of the copending application is, however, a homogeneous catalyst and generally can not be practically used for gas phase polymerization. The use of a

supported catalyst offers the possibility of gas phase compatibility. Control of the particle size distribution of the polymeric product in the various polymerization processes eliminates or reduces the extent of reactor fouling.

Supported catalysts for olefin polymerization are well known in the art. These catalysts offer, among others, the advantages of being usable in gas or slurry phase reactors allowing the control of polymer particle size and thereby the control of product bulk density. Gas phase reactors also eliminate the need for a solvent and the equipment for solvent handling and separation. However, the known Ziegler-Natta olefin polymerization supported catalysts also present disadvantages which include broad MWD and composition distribution (CD), inefficient incorporation of comonomers, poor sequence distribution and, in the case of lower activity catalysts, the need for a product deashing step.

Supported metallocene-alumoxane catalysts for olefin polymerization are described in U.S. Patent 4,701,432 of Welborn. These supported metallocene-alumoxane catalysts are obtained by reacting a metallocene and an alumoxane in the presence of the solid support material. The supported catalyst may then be employed either as the sole catalyst component or may be employed in combination with an organometallic cocatalyst. The supported metallocene-alumoxane catalyst, however, still produces polymers of generally lower molecular weight and comonomer incorporation than desired for certain applications.

It would be desirable to provide a supported catalyst for gas or slurry phase olefin polymerization that eliminates the need for either an alumoxane or an alkyl aluminum cocatalyst. It would be further desirable that such supported catalyst be capable of providing a polymer product having a high molecular weight, narrow MWD and CD, good comonomer incorporation, good sequence distribution, high bulk density and controlled particle size for ease of removal from the reactor.

Summary

The invention provides a supported ionic metallocene catalyst which is suitable for use in the polymerization of olefins including gas or slurry phase polymerization of olefins. The heterogeneous catalyst, like its homogeneous counterpart disclosed in our European Patent Application EP 277 004, permits the production of polyolefins of high molecular weight and narrow molecular weight distribution MWD at high rates. Moreover, the polyolefin products of the supported catalyst have a narrow composition distribution (CD) and improved sequence distribution of comonomers as compared to the products of prior art conventional supported Ziegler-Natta catalysts.

The possibility of producing a supported catalyst was surprising since it would have been predicted that the reaction of ionic catalyst as described in the copending application with a Lewis base such as is present on a metal oxide surface would result in catalyst deactivation. This invention is even more surprising since aluminum alkyls are not present during catalyst preparation and furthermore the polymer products are similar to that obtained with the unsupported catalyst.

The supported ionic metallocene catalyst of this invention comprises the ionic metallocene catalyst and a suitable support material. The metallocene component of the ionic metallocene catalyst may be selected from a bis(cyclopentadienyl) derivative of a Group IV-B (Periodic Table of Elements, published and copyrighted by CRC Press, Inc., 1984) metal compound containing at least one ligand which will combine with an activator component or at least a portion thereof such as a cation portion thereof. The activator component is an ionic compound comprising a cation which will irreversibly react with at least one ligand contained in said Group IV-B metal compound (metallocene component) and an anion which is a single coordination complex comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central formally charge-bearing metal or metalloid atom, which anion is bulky, labile and

stable to any reaction involving the cation of the activator component. The charge-bearing metal or metalloid may be any metal or metalloid capable of forming a coordination complex which is not hydrolyzed by aqueous solutions. Upon combination of the metallocene component, and activator component, the cation of the activator component reacts with one of the ligands of the metallocene component, thereby generating an ion pair consisting of a Group IV-B metal cation with a formal coordination number of 3 and a valence of +4 and the aforementioned anion, which anion is compatible with and noncoordinating toward the metal cation formed from the metallocene component. The anion of the activator compound must be capable of stabilizing the Group IV-B metal cation complex without interfering with the ability of the Group IV-B metal cation or its decomposition product to function as a catalyst and must be sufficiently labile to permit displacement by an olefin, diolefin or an acetylenically unsaturated monomer during polymerization.

Either the ionic metallocene catalyst or both its components will be contacted with an inorganic or organic solid support material, thermally or chemically dehydrated before such contact, and treated with a trailkylaluminum solution, to form the supported ionic metallocene catalyst of this invention.

The method for preparing these supported ionic catalyst comprises the steps of,

(a) combining, in a solvent or diluent

(i) at least one metallocene component comprising a bis(cyclopentadienyl) metal compound containing at least one ligand capable of reacting with a proton, said metal being selected from Group IV-B metals,

(ii) at least one activator component comprising a cation capable of donating a proton and an anion, said anion being a single coordination complex comprising a plurality of lipophilic radicals covalenty coordinated to and shielding a central charge-bearing metal or metalloid atom, said anion being bulky, labile and capable of stabilizing the metal cation formed as a result of reaction between the two, and